International Journal of Thermophysics, Vol. 14, No. 1, 1993

Liquid Viscosities and Densities of HFC-134a + Glycol Mixtures

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Received October 13, 1992

Liquid viscosity and density of six binary mixtures of HFC-134a with glycols [ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol (400), and polypropylene glycol (2000)] have been measured in the temperature range from 273 to 333 K. The viscosity was measured by a rolling-ball viscometer calibrated with standard liquids of viscosities and densities (JS5, JS10, JS20, and JS50). The density was measured with a glass pycnometer. The uncertainties of the measurements were estimated to be less than 3.4% for viscosity and 0.04% for density, respectively. An equation is given to represent the obtained viscosity values as a function of weight fraction and temperature.

KEY WORDS: density; diethylene glycol; ethylene glycol; HFC-134a; polyethylene glycol; polypropylene glycol; tetraethylene glycol; triethylene glycol; viscosity.

1. INTRODUCTION

Precise information on thermophysical properties of the mixtures of new refrigerants with refrigerant oils is required to select desirable refrigerant oils [1]. HFC-134a is one of the environmentally acceptable alternative refrigerants of recent interest. However, there are only a few studies reported in the literature which present the thermophysical properties of the mixtures, such as viscosity and density, that affect the mechanical system of a refrigerator.

In the present work, the viscosity and density of mixtures of HFC-134a with glycols (model substances of refrigerant oils) were measured in the temperature range from 273 to 333 K.

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0195-928X/93/0100-0045$07.00/0

2. EXPERIMENTAL

2.1. Materials

The six glycols and HFC-134a were supplied as the reagent grade from commercial sources. The purities of ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, and HFC-134a were 99, 99, 99, 95, and 99.9%, respectively. The average molecular weights of polyethylene glycol and polypropylene glycol were 400 and 2000. The reagents were used without any further purification.

2.2. Measurement

The rolling-ball viscometer used in this work is shown in Fig. 1. It can measure a wide range of viscosity of the mixtures of HFC-134a with glycol by changing the ball density and the angle of the inclination of the glass tube. The viscometer was located in a water bath whose temperature was regulated to within ±30 mK of a set-point temperature. The temperature was measured with standard mercury thermometers calibrated by the National Research Laboratory of Metrology, Japan, within an accuracy of ±30 mK. The uncertainty in the viscosity resulting from an absolute accuracy of temperature measurement is estimated to be less than 0.7% for polypropylene glycol (2000) at 273.15 K. The rolling time of a glass or a steel ball (1.00-cm diameter) in a glass tube (1.05-cm internal diameter)

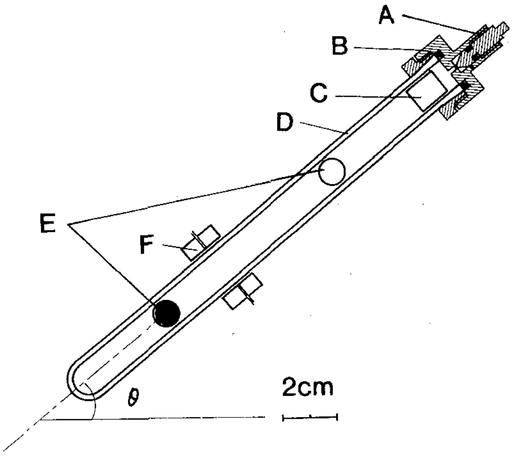

Fig. 1. Rolling-ball viscometer: A, valve; B, joint; C, separator; D, glass tube; E, rolling ball; F, optical detector.

filled with a sample liquid is related to the viscosity η, in mPa · s, as follows:

$$\eta = K \sin \theta (\rho_0 - \rho) t \tag{1}$$

where K is the viscometer constant, θ is the angle of inclination of the tube from horizontal in degrees, and ρ and ρ_0 are the densities of liquid and ball in kg · m^{-3}. The time was monitored with an optical detector [2]. When the ball passes over the detector, the voltage of the detector changes because of the laser intensity. The rolling time, ranging from 0.6 to 15 s, was recorded by detecting the change in the voltage with an electric counter with a reproducibility of 2%. The angle of inclination θ was fixed between 30 and 56° with an accuracy of 0.5%. The viscometer constant K was determined by calibrating with standard liquids of viscosities and densities (JS5, JS10, JS20, and JS50) between 293 and 313 K with an accuracy of 0.6%. The accuracy of the calculated viscosities was estimated to be 3.4%. The measurements were performed at Reynolds numbers of less than 15, according to the method of Hubberd and Brown [3]. Densities of six binary mixtures of HFC-134a and glycols were measured with the glass pycnometer described in detail elsewhere [4] with an accuracy of 0.04%, except for pure HFC-134a, which were literature data [5] measured in a similar manner with an accuracy of ±0.3%.

3. RESULTS

Density values for glycol monomers in the present work agree with the literature data [6, 7] within 0.4% as shown in Fig. 2. The viscosity values

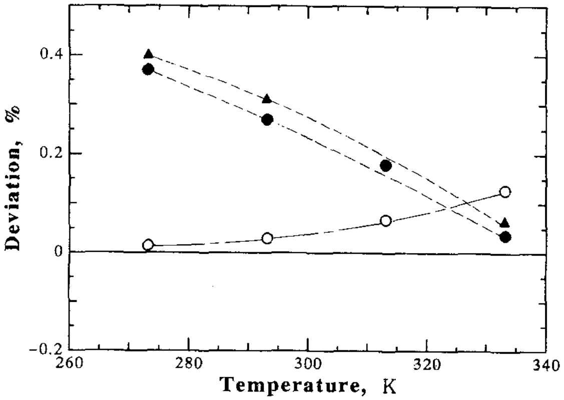

Fig. 2. Deviations for density between the literature data and the present work. Deviation = $100[(\rho_{\text{lit.}} - \rho_{\text{present work}})/\rho_{\text{present work}}]$. (○) Ethylene glycol; (●) diethylene glycol; (▲) triethylene glycol; (-----) Obermeier et al. [6]; (———) Marchetti et al. [7].

Table I. Densities of HFC-134a + Glycol Mixtures

T (K)							
273.15		293.15		313.15		333.15	
x	ρ ($\mathrm{kg \cdot m^{-3}}$)	x	ρ ($\mathrm{kg \cdot m^{-3}}$)	x	ρ ($\mathrm{kg \cdot m^{-3}}$)	x	ρ ($\mathrm{kg \cdot m^{-3}}$)
HFC-134a + ethylene glycol							
0	1294.5[a]	0	1225.4[a]	0	1147.2[a]	0	1052.7[a]
0.972	1134.0	0.972	1120.2	0.972	1105.3	0.972	1089.5
0.961	1136.1	0.961	1122.0	0.961	1108.3	0.961	1092.1
1	1126.9	1	1113.1	1	1099.0	1	1084.7
HFC-134a + diethylene glycol							
0.825	1166.9	0.826	1152.6	0.826	1132.1	0.826	1116.6
0.933	1144.6	0.933	1129.2	0.934	1113.8	0.934	1098.7
1	1129.8	1	1115.8	1	1101.4	1	1087.4
HFC-134a + triethylene glycol							
0.728	1194.6	0.728	1174.5				
0.764	1186.9	0.764	1168.8	0.765	1147.6	0.765	1128.4
0.817	1176.3	0.817	1157.9	0.817	1139.2	0.817	1121.1
0.911	1156.7	0.911	1139.9	0.911	1121.3	0.911	1104.6
1	1139.0	1	1123.3	1	1108.0	1	1092.5
HFC-134a + tetraethylene glycol							
0.655	1211.2	0.655	1187.7	0.655	1164.0		
0.715	1197.9	0.715	1175.8	0.715	1154.1	0.715	1133.3
0.890	1160.9	0.891	1142.7	0.891	1124.5	0.891	1107.4
1	1139.6	1	1123.1	1	1107.9	1	1091.9
HFC-134a + polyethylene glycol (400)							
0.458	1254.9	0.458	1222.1				
0.556	1237.2	0.557	1209.0	0.557	1181.2		
0.702	1205.7	0.702	1182.5	0.703	1159.3	0.703	1136.9
0.843	1175.5	0.843	1156.1	0.843	1137.0	0.843	1118.2
1	1141.3[b]	1	1124.7	1	1108.3	1	1092.5
HFC-134a + polypropylene glycol (2000)							
0.329	1196.2	0.329	1162.2				
0.428	1179.4	0.428	1147.3	0.428	1114.1		
0.538	1143.9	0.538	1116.6	0.538	1091.8	0.538	1061.3
0.695	1104.7	0.695	1081.1	0.695	1058.2	0.695	1036.2
0.805	1081.5	0.805	1059.1	0.805	1041.7	0.695	1022.8
1	1018.3	1	1002.9	1	987.3	1	972.4

[a] From Ref. 5.

[b] Extrapolated value.

Table II. Viscosities of HFC-134a + Glycol Mixtures

T (K)							
273.15		293.15		313.15		333.15	
x	η (mPa · s)	x	η (mPa · s)	x	η (mPa · s)	x	η (mPa · s)
HFC-134a + ethylene glycol							
0	0.2728[a]	0	0.2139[a]	0	0.1697[a]	0	0.1354[a]
		0.948	16.9	0.949	7.76	0.950	4.33
0.964	50.4	0.964	17.1	0.965	7.91	0.966	4.32
0.974	52.8	0.974	17.9	0.975	7.86	0.976	4.39
1	55.9	1	19.2	1	8.45	1	4.75
HFC-134a + diethylene glycol							
0.787	35.1	0.788	12.4				
		0.814	14.3	0.816	6.78	0.817	3.92
0.843	50.0	0.844	16.7	0.845	7.29	0.846	4.14
0.892	67.9	0.892	21.0	0.893	8.26	0.895	4.27
1	117.8	1	33.6	1	12.8	1	6.02
HFC-134a + triethylene glycol							
0.731	32.1	0.732	11.3	0.733	5.52		
0.789	47.3	0.790	15.8	0.791	7.14	0.792	3.77
0.901	98.1	0.901	28.9	0.903	11.2	0.904	5.71
1	164.0	1	46.1	1	17.4	1	9.09
HFC-134a + tetraethylene glycol							
0.697	27.1	0.698	9.94	0.700	4.99	0.702	2.96
0.818	70.1	0.820	21.1	0.821	9.21	0.823	4.96
0.887	109.0	0.888	32.9	0.889	13.5	0.890	6.89
1	208.8	1	57.4	1	22.8	1	11.8
HFC-134a + polyethylene glycol (400)							
0.495	10.1	0.496	4.43				
0.609	26.1	0.610	9.99	0.612	5.14	0.614	3.07
0.694	59.4	0.695	20.2	0.697	9.73		
0.754	94.1	0.756	29.9	0.757	13.2	0.759	7.22
0.865	197.6	0.865	55.4	0.866	23.1	0.867	12.2
1	432.9[b]	1	120.1	1	44.4	1	21.6
HFC134a + polypropylene glycol (2000)							
0.514	14.7	0.515	5.97	0.515	3.56		
0.525	16.8	0.526	6.68				
0.636	46.2	0.637	19.6	0.639	10.8	0.640	6.68
0.718	103.5	0.718	39.7	0.720	19.1	0.721	12.4
0.837	347.6	0.839	106.8	0.843	46.7	0.846	24.4
1	2024	1	429.6	1	143.5	1	62.9

[a] From Ref. 2.

[b] Extrapolated value.

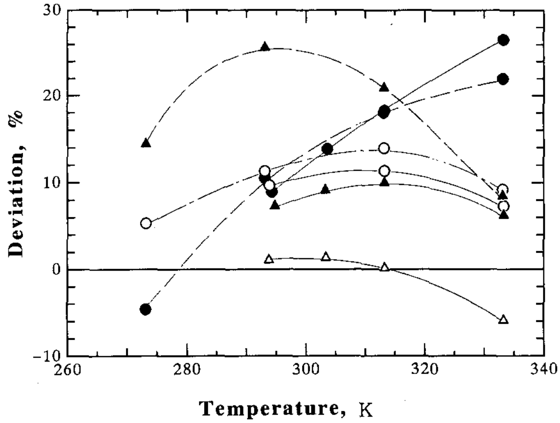

Fig. 3. Deviations for viscosity between the literature data and the present work. Deviation $= 100[(\eta_{\text{lit.}} - \eta_{\text{present work}})/\eta_{\text{present work}}]$. (○) Ethylene glycol; (●) diethylene glycol; (▲) triethylene glycol; (△) tetraethylene glycol; (----) Obermeier et al. [6]; (— — —) Marchetti et al. [7]; (——) Lee and Teja [8].

Table III. Constants in Eqs. (3), (4), and (5) and Deviation of Experimental Viscosity Data from Eq. (2)[a]

	HFC-134a + EG	HFC-134a + DiEG	HFC-134a +TriEG	HFC-134a +TetraEG	HFC-134a +PEG	HFC-134a +PPG
$-a_1$	8.3589	−3.2773	3.7539	3.4391	1.7405	−13.3349
$10^2 a_2$	2.0940	−1.3754	1.1424	1.1694	0.4227	−3.9902
$-10^{-1} b_1$	0.48814	1.9545	1.2505	1.2924	1.6157	3.4616
$10^2 b_2$	0.8480	5.1548	2.5213	2.4465	3.4670	8.5812
$-10^{-1} c_1$	4.1936	3.9966	5.3588	5.5316	4.5474	6.1350
$10^{-4} c_2$	0.85863	0.87443	1.07922	1.10646	0.97882	1.27147
$10^2 c_3$	5.3190	4.6576	7.0232	7.3770	5.7529	8.2052
Av. dev. (%)[b]	1.3	2.3	3.7	5.0	8.3	7.6
Max. dev. (%)[c]	2.8	8.0	8.7	12.1	21.0	15.3

[a] EG, ethylene glycol; DiEG, diethylene glycol; TriEG, triethylene glycol; TetraEG, tetraethylene glycol; PEG, polyethylene glycol (400); PPG, polypropylene glycol (2000).

[b] $100[(\sum |\eta_{\text{exp}} - \eta_{\text{calc}}|/\eta_{\text{calc}})/n]$.

[c] Maximum of $100(|\eta_{\text{exp}} - \eta_{\text{calc}}|/\eta_{\text{calc}})$.

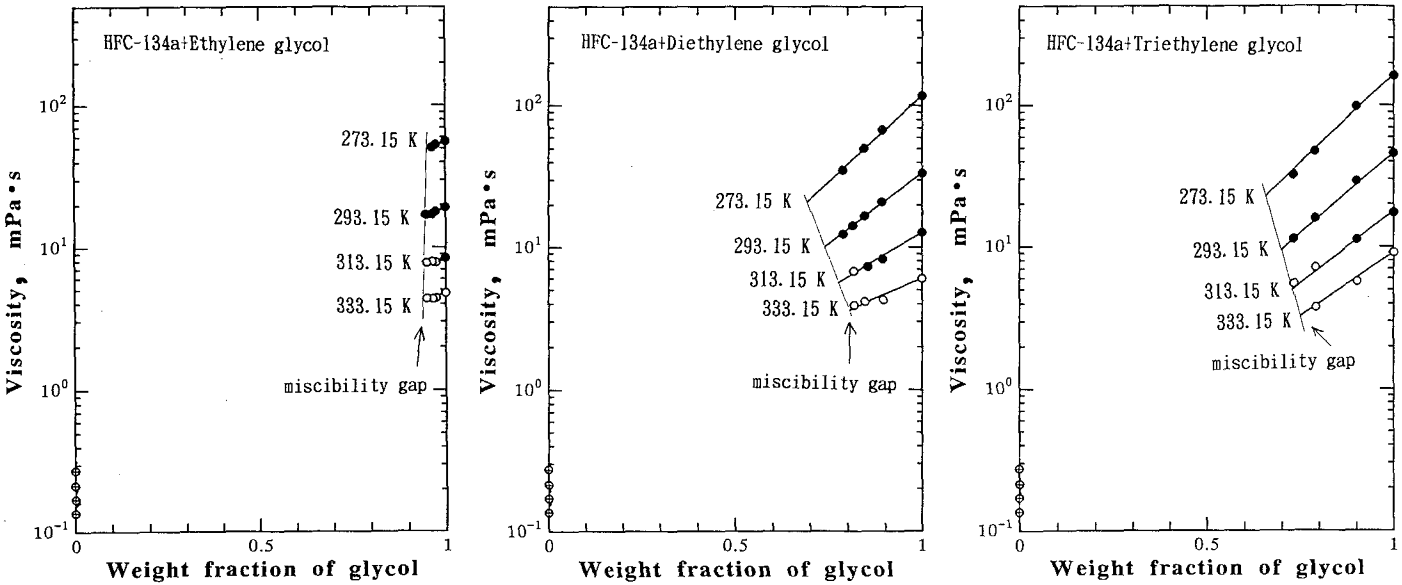

Fig. 4. Liquid viscosities of HFC-134a–ethylene glycol, –diethylene glycol, and –triethylene glycol mixtures. (●) Measured with a steel ball; (○) measured with a glass ball; (⊕) measured with a capillary viscometer [2]; (——) Eq. (2) with Eqs. (3), (4), and (5).

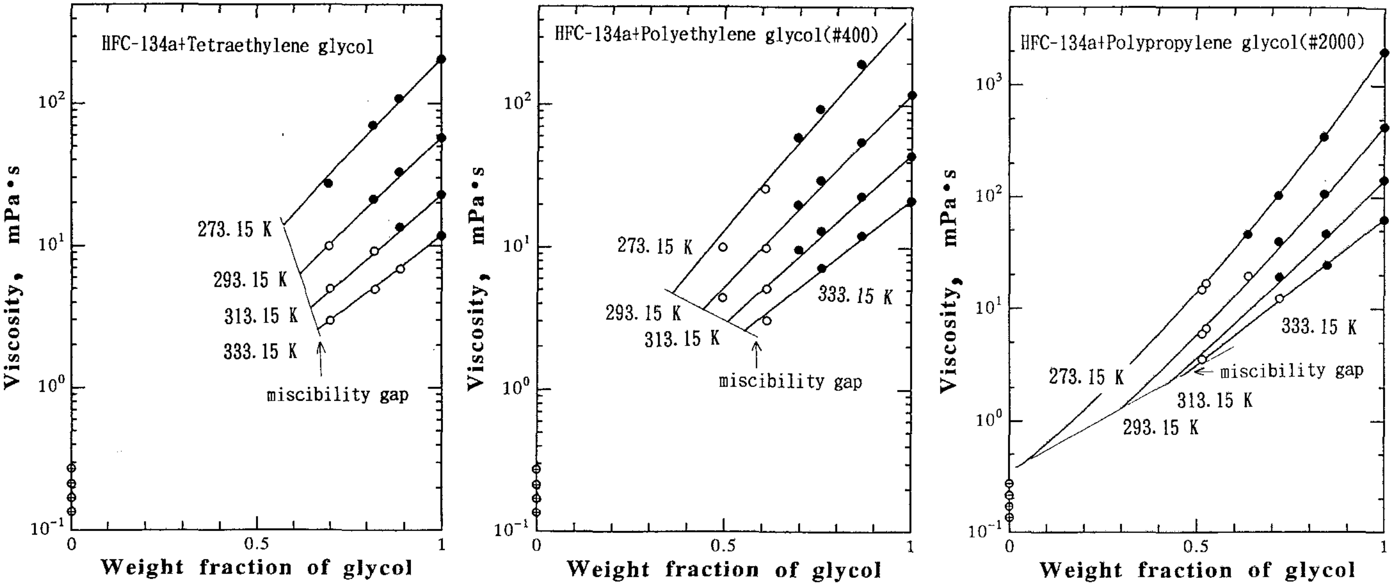

Fig. 5. Liquid viscosities of HFC-134a–tetraethylene glycol, –polyethylene glycol (400), and –polypropylene glycol (2000) mixtures. (●) Measured with a steel ball; (○) measured with a glass ball; (⊕) measured with a capillary viscometer [2]; (——) Eq. (2) with Eqs. (3), (4), and (5).

deviate considerably except for tetraethylene glycol, obtained by Lee and Teja [8] as shown in Fig. 3. In Tables I and II, the experimental data are listed for the density and viscosity of six binary mixtures of HFC-134a with glycols. HFC-134a has a limited miscibility for glycols, which decreases with a decrease in molecular weight of glycols as shown in Figs. 4 and 5. The viscosity of all the mixtures decreases significantly with an increase in the weight fraction of HFC-134a toward those of the pure refrigerant.

The obtained viscosity values η, in mPa · s, were fitted according to the following equation, which started from the viscosity of pure glycol at each isotherm because of the existence of the miscibility gap:

$$\ln(\eta/\eta_0) = a(1-x)^2 + b(1-x) \tag{2}$$

with

$$\eta_0 = \exp(c_1 + c_2/T + c_3 T) \tag{3}$$

$$a = a_1 + a_2 T \tag{4}$$

$$b = b_1 + b_2 T \tag{5}$$

where η_0 is the viscosity of pure glycol in mPa · s and x is its weight fraction, while a_1, a_2, b_1, b_2, c_1, c_2, and c_3 are adjustable parameters, and T is temperature in K, respectively.

The constants in Eqs. (3), (4) and (5) as well as the deviations of the experimental data from Eq. (2) are listed in Table III. It may be seen that the deviations increase with increasing molecular weight of the glycols.

ACKNOWLEDGMENT

We thank Mr. K. Nishi for valuable discussions and for his help in general.

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